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# The influence of steps on the dissociation of NO on Pt surfaces: Temperature-programmed desorption studies of NO adsorption on Pt{211}

R. J. Mukerji, A. S. Bolina, and W. A. Brown<sup>a)</sup>

*Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom*

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Temperature-programmed desorption (TPD) has been used to investigate the adsorption of NO on Pt{211} at 300 K and 120 K. Results show that NO dissociation occurs readily on Pt{211}, as evidenced by the observation of N<sub>2</sub> and N<sub>2</sub>O in the TPD spectrum. Following adsorption at 120 K three NO TPD peaks at 338, 416, and 503 K are observed, in agreement with previous observations. In combination with data acquired in a recent reflection absorption infrared spectroscopy and density functional theory investigation of NO/Pt{211}, these peaks are assigned to the desorption of NO from an O–NO complex, the recombinative desorption of N and O atoms, and to desorption of a step-bridged NO species, respectively. These assignments are in disagreement with previous work, where the high-temperature NO peak was assigned to the desorption of step bound NO and the two low-temperature peaks were assigned to the desorption of NO from terrace sites. TPD spectra recorded following adsorption at 300 K, with a heating rate of 1 K s<sup>−1</sup>, show similar features to those recorded following 120 K adsorption. This is also in disagreement with previous observations, where only two NO TPD peaks were observed following adsorption at room temperature. This disagreement can be accounted for by the different heating rates used in the two experiments. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619940]

## I. INTRODUCTION

Many studies of the adsorption and dissociation of NO on Pt surfaces have been undertaken in the past.<sup>1</sup> It is generally accepted that Pt{111} and Pt{110} are inactive for NO dissociation, while NO dissociates on Pt{100} at room temperature. Stepped-kinked surfaces composed of {100} step sites and {111} terraces, such as Pt{210}, Pt{310}, and Pt{410},<sup>2–6</sup> have also been shown to dissociate NO at room temperature.

Pt{211} consists of three-atom-wide terraces of {111} structure, separated by one-atom-high steps of {100} character. Due to the presence of the step sites, it is expected that Pt{211} will bind NO more strongly than a flat surface like Pt{111}. In addition, it is expected that the stepped Pt{211} surface may be more active for NO dissociation than the equivalent flat Pt{111} surface. However, there is still some controversy in the literature concerning the dissociation of NO on Pt{211} at 300 K. Banholzer and co-workers<sup>7</sup> used symmetry considerations to show that Pt{111} surfaces with {100} steps, such as Pt{211}, should show high activity for NO dissociation at the step sites. However, Sugisawa *et al.*<sup>8</sup> found that NO did not dissociate on Pt{211} until ~480 K. Gohndrone and Masel<sup>9</sup> noted that Pt{211} dissociates NO with a similar reactivity to Pt{411} and Pt{100} which is known to dissociate NO at room temperature.<sup>10</sup> Previous work by Heiz<sup>11,12</sup> did not look for NO dissociation on Pt{211}, but work on polycrystalline Pt (Ref. 13) and defect-

covered Pt{111} (Refs. 14 and 15) showed that NO adsorption at 300 K was predominantly molecular. In contrast, a recent reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) investigation which we have performed<sup>16</sup> suggested that NO does dissociate on Pt{211} at 300 K.

To try to investigate this apparent contradiction further, we have performed an extensive study of the NO on Pt{211} adsorption system. Here we present temperature-programmed desorption (TPD) data for this system. We have also undertaken a RAIRS and DFT investigation of this adsorbate system. The results of this investigation are reported in detail elsewhere.<sup>16</sup> As the Pt{211} surface contains terraces of {111} structure, we have compared our results to those previously obtained for NO adsorption on Pt{111} to help to determine the role that the steps play in NO adsorption and dissociation.

NO adsorption has been extensively investigated on the flat Pt{111} surface and has been found to be entirely molecular. TPD studies<sup>17–24</sup> all show similar desorption spectra. Adsorption at 95 K leads to the production of three NO TPD peaks at 190, 320, and 350 K. The two higher-temperature peaks have been assigned to the desorption of atop and bridged NO species, respectively.<sup>24</sup> No assignment of the low-temperature peak has been made. Some authors have also observed a small amount of N<sub>2</sub> desorption. This was thought to be due to the presence of defects on the Pt{111} surface which caused the NO to dissociate during the TPD experiment.

In contrast, there are very few previous experimental

<sup>a)</sup>Author to whom correspondence should be addressed. Fax: +44 20 7679 7463; Electronic mail: w.a.brown@ucl.ac.uk

TABLE I. A summary of the observed RAIR bands, and the band assignments, for NO adsorbed on Pt{211} (Ref. 16).

Band frequency ( $\text{cm}^{-1}$ )	Adsorption temperature (K)	Band assignment
1801	307	O–NO complex
1609	307	Step-bridged NO affected by O atoms
1576	307	Step-bridged NO
1688	120	Top-terrace NO
1620	120	Step-bridged NO

studies of the adsorption of NO on Pt{211}.<sup>8,9,11,12,16,25</sup> Heiz performed RAIRS investigations of electron<sup>11,12</sup> and photon<sup>11</sup> stimulated desorption of NO from the step sites of Pt{211}. They observed infrared bands due to NO adsorbed on both step and terrace sites. NO adsorption on Pt{211} has also been studied using TPD,<sup>8,9</sup> ultraviolet photoelectron spectroscopy (UPS),<sup>8</sup> and x-ray photoelectron spectroscopy (XPS).<sup>8</sup> Sugisawa and co-workers<sup>8</sup> used XPS and UPS to show that NO adsorbs molecularly on Pt{211} at 95 K.

TPD spectra following NO adsorption on Pt{211} at 95 K (Ref. 8) resulted in the desorption of three NO species with desorption temperatures of 303, 378, and 488 K. The high-temperature peak grew into the spectrum first and the two lower-temperature peaks were observed to grow in with increasing NO coverage. The high-temperature peak was assigned to desorption of NO from the step sites and the two lower-temperature peaks were assigned to desorption from the {111} terraces.<sup>8</sup> In addition to the desorption of NO, N<sub>2</sub> desorption was also detected in the TPD spectrum. The production of N<sub>2</sub> was assigned to the recombinative desorption of N atoms, produced by NO dissociation on the Pt{211} surface. NO dissociation was thought to occur as a result of heating, rather than on initial adsorption of NO. No desorption of molecular O<sub>2</sub> was seen in the TPD when NO was adsorbed onto a clean Pt{211} surface. O<sub>2</sub> desorption was only observed after repeated cycles of NO dosing and desorption. It was concluded that O atoms, produced by NO dissociation, diffuse into the subsurface region on heating. Only after all subsurface sites had been saturated was it possible to see the desorption of O<sub>2</sub> at 860 K in the TPD spectrum.<sup>8</sup>

Gohndrone and Masel<sup>9</sup> performed TPD investigations of the adsorption of NO on Pt{211} following adsorption at 300 K. Two NO peaks, at 370 and 500 K, were observed in the TPD spectrum. It was speculated that the low-temperature peak occurred due to desorption from the terraces and the high-temperature peak was due to desorption of NO from the step sites. A peak due to the desorption of N<sub>2</sub>, at 450–500 K, was also observed in the TPD spectrum. TPD spectra resulting from the desorption of NO from polycrystalline Pt (Refs. 13 and 26) and stepped Pt{111} (Refs. 14 and 15) surfaces have also been recorded.

TPD investigations of NO adsorption have also been performed for Pt{533} (Refs. 27–29). Pt{533} has a very similar structure to Pt{211}—it consists of four-atom-wide terraces of {111} structure separated by one-atom-high steps of {100} character. TPD following adsorption of NO on Pt{533} at 95 K gave rise to four NO peaks at 243, 307, 385,

and 504 K and one N<sub>2</sub> peak at 520 K (Ref. 27). The three low-temperature peaks were assigned to NO desorption from terraces and the high-temperature NO peak was assigned to NO desorption from step sites.

We have performed an extensive RAIRS and DFT investigation of the adsorption of NO on Pt{211}. The results of this study are pertinent to the data presented here, and hence a brief summary of our findings is given below. A more detailed description of these data can be found elsewhere.<sup>16</sup> RAIRS experiments showed that NO adsorption on Pt{211} is very complex and is strongly temperature dependent. Adsorption of NO at 307 K up to saturation coverage resulted in three bands in the RAIR spectrum at 1801, 1609, and 1576  $\text{cm}^{-1}$ . When this surface was heated, the band at  $\sim 1800 \text{ cm}^{-1}$  was the first to disappear from the RAIR spectra at 350 K. Further heating caused the two peaks at 1609 and 1576  $\text{cm}^{-1}$  to merge into one peak, which then disappeared from the spectrum by 450 K. When adsorption took place at 120 K, only two bands were seen at 1688 and 1620  $\text{cm}^{-1}$ . The bands observed at 300 K at 1801 and 1576  $\text{cm}^{-1}$  were not seen on adsorption at 120 K. However, heating a surface saturated with NO at 120 K resulted in the appearance of the band at 1801  $\text{cm}^{-1}$  at temperatures above 230 K. At the same time, the peak at 1688  $\text{cm}^{-1}$  disappeared from the spectrum. The peak at 1801  $\text{cm}^{-1}$ , which appeared following heating to 230 K, disappeared from the spectrum following heating to 360 K. The peak at  $\sim 1600 \text{ cm}^{-1}$  was again the last to disappear from the RAIR spectrum at 450 K.

To help with the assignment of the observed vibrational bands, DFT calculations were also performed. The calculations showed that a bridged species, bonded to the step edge, is the most stable NO species on the Pt{211} surface. The calculations also showed that the temperature dependence of NO adsorption on Pt{211} could be assigned to NO dissociation, which occurs on the step sites at room temperature but not at 120 K. The calculations identified a new species, an O–NO complex, which is formed on the surface as a result of NO dissociation at room temperature. This species is formed by the reaction of NO with an O atom bonded to a step-bridge site. The calculated energy of the bond between the NO and the O atom is 68  $\text{kJ mol}^{-1}$ . This species gives rise to the band seen in the 300 K RAIR spectrum at 1801  $\text{cm}^{-1}$ . A full assignment of all of the observed infrared bands, which was made both by comparison of the observed vibrational frequencies with previous data<sup>11–13,15,26</sup> and with our calculated vibrational frequencies,<sup>16</sup> is given in Table I.



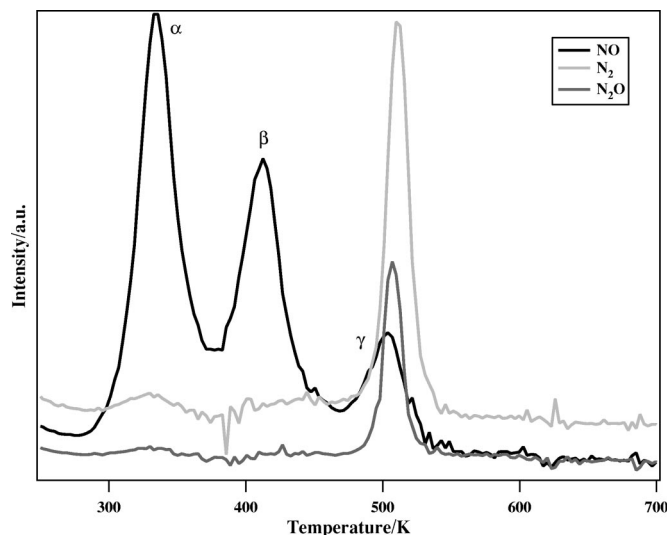


FIG. 1. TPD spectra recorded following a 4 L dose of NO onto Pt{211} at 120 K. The spectra shown are for the desorption of masses 28 ( $N_2$ ), 30 (NO), and 44 ( $N_2O$ ). The heating rate was  $8\text{ K s}^{-1}$ .

## II. METHODOLOGY

Experiments were performed in an ultrahigh-vacuum (UHV) chamber that has a base pressure of  $\leq 2 \times 10^{-10}$  mbar. The Pt{211} crystal was cleaned by repeated cycles of Ar ion sputtering at 300 K, oxygen treatment at 900 K in  $5 \times 10^{-8}$  mbar  $O_2$ , and annealing at 1050 K. Sample cleanliness was confirmed by observation of the expected low-energy electron diffraction (LEED) pattern for Pt{211} and by the production of the expected TPD spectrum following a saturation exposure of CO on Pt{211} (Refs. 30 and 31). NO (99.5% purity, BOC Ltd.) was admitted into the chamber by means of a high-precision leak valve. Doses, in Langmuir ( $1\text{ L} = 10^{-6}$  Torr s), were calculated without correction of the ion gauge for NO. TPD data were recorded using a Hidden Analytical HAL201 quadrupole mass spectrometer. Spectra were recorded at heating rates of 1 and  $8\text{ K s}^{-1}$ .

## III. RESULTS AND DISCUSSION

### A. 120 K adsorption

Figure 1 shows TPD spectra which result from a saturation dose of NO on the Pt{211} surface at 120 K. Three peaks, labeled  $\alpha$ ,  $\beta$ , and  $\gamma$ , are seen in the NO spectrum at 338, 416, and 503 K, respectively. Desorption peaks for masses 28 ( $N_2$ ) and 44 ( $N_2O$ ) are also observed. The  $N_2$  and  $N_2O$  desorption peaks occur in coincidence with each other with a desorption temperature of 510 K. The high-temperature NO peak, labeled  $\gamma$ , occurs just to the low-temperature side of these two peaks. These NO TPD spectra are in good agreement with those observed by Sugisawa *et al.*,<sup>8</sup> although no  $N_2O$  desorption was reported previously. Three TPD peaks were also observed following NO adsorption on Pt{111} at 95 K (Refs. 17–24). However, the peaks all occurred at much lower temperatures on Pt{111}, and therefore it is unlikely that any of the species desorbing from Pt{211} are the same as those observed for Pt{111}.

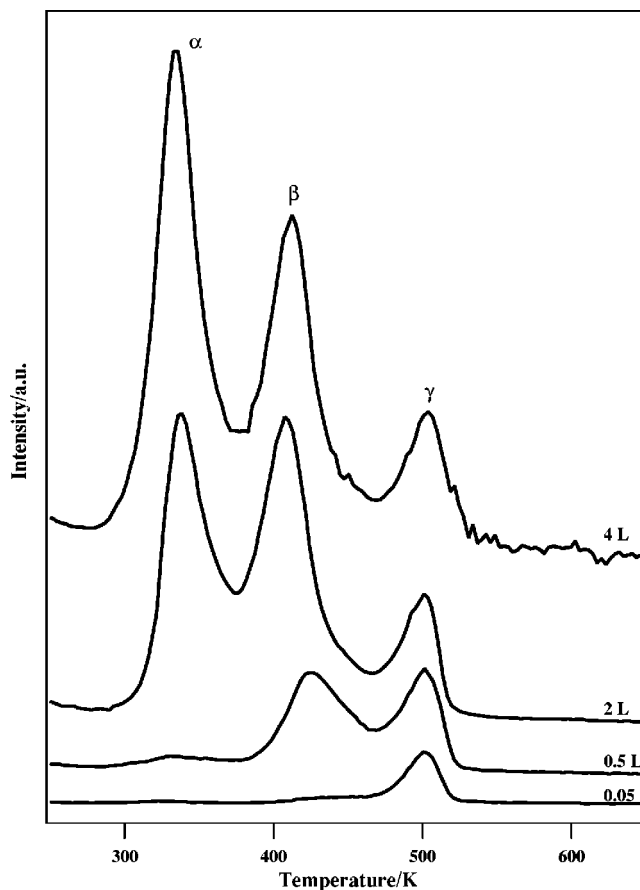


FIG. 2. NO TPD spectra recorded at a heating rate of  $8\text{ K s}^{-1}$  following exposure of a Pt{211} surface held at 120 K to various doses of NO.

Figure 2 shows the way in which the three NO peaks seen in Fig. 1 grow into the TPD spectrum as a function of increasing NO dose at 120 K. The  $\gamma$  peak grows into the spectrum first, following an NO exposure of 0.05 L, and is observed at a desorption temperature of 503 K. This peak grows in intensity with increasing NO exposure; however, the peak temperature remains constant. With further NO exposure a second peak, labeled  $\beta$ , grows into the spectrum at 424 K. This peak also increases in intensity with increasing NO exposure and shifts down in temperature slightly to reach 416 K at saturation. The final peak that grows in is that labeled  $\alpha$ , which grows in at 338 K and grows to dominate the spectrum at saturation. The way in which the desorption peaks for masses 28 ( $N_2$ ) and 44 ( $N_2O$ ) change with increasing NO exposure is not shown here, but measurements show that both of these peaks increase in intensity with increasing NO dose. The desorption of  $N_2$  and  $N_2O$  is observed even following very low exposures of NO on the Pt{211} surface. In agreement with previous experiments,<sup>8</sup> desorption of mass 32 ( $O_2$ ) is not observed at any NO exposure for desorption temperatures up to 1000 K.

The observation of desorption peaks due to mass 30, NO, in the TPD spectrum shows that adsorption of NO on Pt{211} is, at least partly, molecular. However, as we will show below, there is also evidence for NO dissociation on Pt{211}. The first NO desorption peak to be observed in the TPD spectra shown in Fig. 2 is that labeled  $\gamma$ . This peak appears at a desorption temperature of 503 K. The tempera-

ture of this peak does not shift with increasing NO exposure on the surface, suggesting that the species giving rise to this peak is desorbing via a first-order process. Our previous RAIRS and DFT investigation of this adsorption system<sup>16</sup> showed that the most stable species on the Pt{211} surface is a bridged NO species bonded to the step edge. This is the only species to be observed in the RAIR spectra following low NO doses and, following annealing, remains on the surface to the highest temperature (450 K). Hence the highest-temperature NO peak, labeled  $\gamma$ , is assigned to the desorption of bridged NO molecules bonded to the Pt{211} step edge. This assignment is in agreement with that of Sugisawa *et al.*<sup>8</sup> who assigned their highest-temperature NO TPD peak to desorption of NO from the step sites of Pt{211}.

The species which gives rise to the peak labeled  $\alpha$  in the NO TPD spectrum (Figs. 1 and 2) is obviously due to the most weakly bound NO species on the Pt{211} surface. This species is observed to desorb at 338 K. This peak has previously been assigned to the desorption of an NO terrace species,<sup>8</sup> the exact nature of which was unknown. However, our recent RAIRS and DFT investigation of this adsorption system<sup>16</sup> showed that the least stable NO species on the Pt{211} surface is an O–NO complex, which forms as a result of NO dissociation. This species is not observed on initial adsorption at 120 K, but is observed to form when the saturated NO adlayer formed at 120 K is heated above 230 K. Calculations show that the bond between the NO and the adsorbed O atom has an energy of only 68 kJ mol<sup>-1</sup> (Ref. 16). Hence the peak labeled  $\alpha$  in the NO TPD spectrum is assigned to the desorption of NO from the O–NO complex which is formed on the Pt{211} surface as a result of NO dissociation. This is in disagreement with previous assignments which suggested that this peak arose due to the desorption of an NO terrace species.<sup>8</sup> The desorption temperature of this peak, 338 K, is in excellent agreement with the temperature at which the band due to the O–NO complex disappears from the RAIR spectra (330–360 K) (Ref. 16). Further evidence for the assignment of this peak to the desorption of NO from an O–NO complex comes from the observation that predosing the Pt{211} surface with O atoms causes the size of this peak to increase, relative to the other TPD peaks, due to increased amounts of the O–NO complex on the surface.<sup>32</sup> The O–NO complex is thought to be bonded to the step edge of Pt{211} as it forms via the bonding of an NO molecule to an O atom adsorbed in a step bridge site.<sup>16</sup>

The only NO TPD peak remaining to be assigned is that labeled  $\beta$  in Figs. 1 and 2. To determine the nature of the  $\beta$ -NO TPD peak it is necessary to consider the NO species that are observed with RAIRS when adsorption occurs at 120 K (Ref. 16). Initial adsorption at 120 K, up to saturation coverage, leads to the observation of bands at 1688 and 1620 cm<sup>-1</sup>. These have been assigned to atop NO on the terrace and to bridged NO on the step edge, respectively.<sup>16</sup> Heating a surface that has been saturated with NO at 120 K, to 230 K, leads to the disappearance of the 1688 cm<sup>-1</sup> band and the appearance of a band at 1801 cm<sup>-1</sup>, assigned to the presence of the O–NO complex. Further heating leads to the disappearance of the 1801 cm<sup>-1</sup> band at  $\sim$ 360 K and to the

disappearance of the 1620 cm<sup>-1</sup> band at 450 K. No other NO species are observed. The  $\alpha$ -NO TPD peak has already been assigned to the desorption of the O–NO complex and the  $\gamma$ -NO peak has been assigned to desorption of the step-bridged NO species. The only other molecular NO species observed with RAIRS, following adsorption at 120 K, is the atop NO species bonded to the terrace which gives rise to the band at 1688 cm<sup>-1</sup> (Ref. 16). However, the  $\beta$ -NO TPD peak cannot be due to this species, as this peak disappears from the RAIR spectrum at  $\sim$ 230 K and the  $\beta$ -NO TPD peak has a desorption temperature of 416 K. Even taking into account the different heating rates used in the TPD experiments and the RAIRS annealing experiments, the  $\beta$ -NO TPD peak cannot be due to desorption of the atop terrace NO species. According to the RAIR spectra, no other molecular NO species are present on the Pt{211} surface. Hence the  $\beta$ -NO peak must either be due to the desorption of an infrared inactive NO species, such as NO bonded with the N–O axis parallel to the surface, or due to the recombinative desorption of N and O atoms which result from NO dissociation. There is no evidence for the presence of an infrared-inactive NO species on Pt{211} either from our own<sup>16</sup> or other<sup>11,12</sup> RAIRS investigations. Hence we assign the  $\beta$ -NO TPD peak to the recombinative desorption of N and O atoms, which result from NO dissociation. While dissociation does not occur at 120 K, the appearance of the 1800 cm<sup>-1</sup> band in RAIRS, assigned to the O–NO complex, is evidence that dissociation does occur on Pt{211} when the surface is heated.<sup>16</sup> Note that, while it has already been shown that NO dissociates on Pt{211} when adsorption occurs at room temperature,<sup>16</sup> the NO dissociation that is observed following adsorption at 120 K occurs when the surface is heated during the TPD experiment.

Further evidence for the assignment of the  $\beta$ -NO TPD peak to recombinative desorption of N and O atoms comes from the observation that predosing the Pt{211} surface with O atoms causes the size of the  $\beta$ -NO TPD peak to decrease<sup>32</sup> due to the blocking of NO dissociation by the preadsorbed O atoms. In addition, the desorption temperature of the  $\beta$ -NO peak decreases slightly with increasing NO exposure, from 424 K at low NO doses to 416 K at saturation. This suggests that this peak may arise due to a second-order desorption process, again in support of our assignment of this peak to an N and O recombination process. This assignment is again in contrast to the previous assignment of this peak to the desorption of an NO terrace bound species.<sup>8</sup> Note that not all of the N and O atoms recombine and desorb as NO since the formation of N<sub>2</sub> and N<sub>2</sub>O, which also requires N atoms, is also observed in the TPD spectrum.

Figure 1 shows the coincident desorption of masses 28 (N<sub>2</sub>) and 44 (N<sub>2</sub>O) at 510 K. The observation of TPD peaks for N<sub>2</sub> and N<sub>2</sub>O is clear evidence that NO dissociation occurs on Pt{211}. In contrast, no N<sub>2</sub> or N<sub>2</sub>O desorption was observed in TPD spectra recorded for the NO/Pt{111} system,<sup>17–24</sup> indicating that dissociation does not occur on this surface. It is therefore assumed that it is the step sites on Pt{211} that cause NO dissociation. The fact that the N<sub>2</sub> and N<sub>2</sub>O TPD peaks are in coincidence suggests that they are formed by the same process. One explanation for this is that

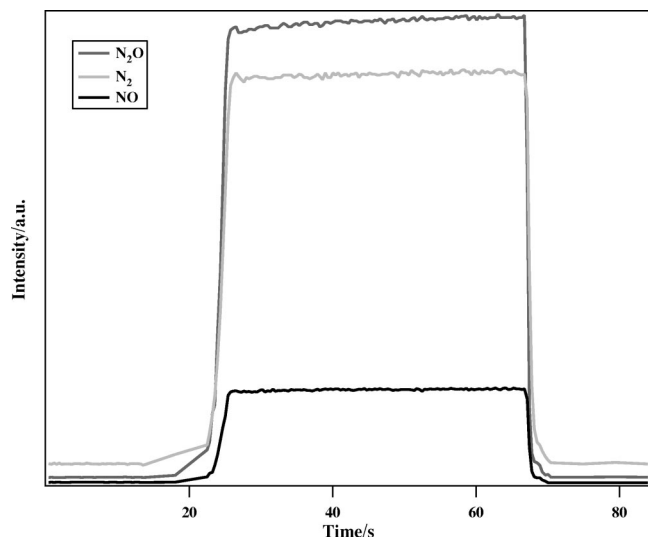


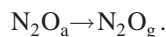
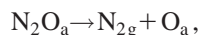
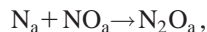
FIG. 3. The cracking pattern that results from an  $\text{N}_2\text{O}$  dose of  $1 \times 10^{-7}$  mbar in the UHV chamber used for the TPD experiments described here. The graph shows the relative intensities measured for masses 28 ( $\text{N}_2$ ), 30 ( $\text{NO}$ ), and 44 ( $\text{N}_2\text{O}$ ).

the  $\text{N}_2\text{O}$  is formed on the surface and subsequent cracking of the  $\text{N}_2\text{O}$  then occurs in the mass spectrometer, producing the observed  $\text{N}_2$ . Figure 3 shows a cracking pattern recorded for  $\text{N}_2\text{O}$ , using the same mass spectrometer that was used in the TPD experiments. It is clear that mass 44,  $\text{N}_2\text{O}$ , is the largest signal and that  $\text{N}_2\text{O}$  cracks into masses 44, 28, and 30 in the approximate ratio of 5:4:1. Examination of Fig. 1 shows that there is a much larger quantity of  $\text{N}_2$  formed in the TPD experiments than that which arises due to  $\text{N}_2\text{O}$  cracking alone. Hence,  $\text{N}_2$  is being formed on the surface during the TPD experiments.

It is possible that  $\text{N}_2$  and  $\text{N}_2\text{O}$  are formed by the reaction of N atoms, formed from NO dissociation, with either another N atom or an NO molecule at the surface. The subsequently formed  $\text{N}_2$  and  $\text{N}_2\text{O}$  would then desorb from the surface immediately. Recombinative desorption of N atoms has previously been suggested to account for  $\text{N}_2$  desorption observed on Pt{211} (Refs. 8 and 9), Pt{533} (Ref. 27), and Pt{111} (Ref. 23). However, if the  $\text{N}_2$  and  $\text{N}_2\text{O}$  are formed by the reaction of N atoms with either another N atom or an NO molecule, then the only way that the TPD peaks could be coincident would be if the formation of both of these species has the same activation barrier. This is unlikely unless the occurrence of both reactions was dictated, for example, by the onset of N atom diffusion on the Pt{211} surface. However if, as suggested, the  $\beta$ -NO TPD peak is due to the recombinative desorption of N and O atoms, then N atoms must already be diffusing around the surface at a lower temperature than that at which  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation is observed.

An alternative explanation for the coincident desorption of  $\text{N}_2$  and  $\text{N}_2\text{O}$  is that the  $\text{N}_2$  is formed directly on the surface from  $\text{N}_2\text{O}$ . The  $\text{N}_2\text{O}$  is formed from the reaction of N atoms with NO, most likely at the step edges. Most of the  $\text{N}_2\text{O}$  that is formed then immediately dissociates to form gas

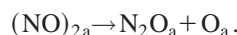
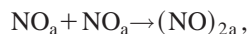
phase  $\text{N}_2$  and adsorbed O atoms. The reactions that could occur would be



This reaction, where  $\text{N}_2\text{O}$  immediately dissociates on formation to give  $\text{N}_2$  and adsorbed O, has previously been observed on Cu{110} (Ref. 33) and Ru{001} (Ref. 34). On Cu{110},  $\sim 50\%$  of the  $\text{N}_2\text{O}$  was thought to dissociate immediately on formation.<sup>33</sup> Due to the presence of the step sites, it might be expected that an even larger proportion of the  $\text{N}_2\text{O}$  might dissociate on Pt{211}. The O atoms which would result from the decomposition of  $\text{N}_2\text{O}$  would bind strongly to the step sites on Pt{211} as shown previously.<sup>35</sup>

It is thought that the  $\text{N}_2\text{O}$  observed in the TPD experiments is formed during the desorption process itself, rather than being formed on the surface at a lower temperature and then desorbing at 510 K. Supporting evidence for this comes from the fact that no peaks due to  $\text{N}_2\text{O}$  are observed with RAIRS at any coverage or at any adsorption temperature.<sup>16</sup> In addition, we investigated the adsorption of  $\text{N}_2\text{O}$  on Pt{211} over the temperature range from 120 to 300 K using RAIRS and TPD. We were not able to see any RAIR spectra or see anything in the TPD spectrum at any adsorption temperature in this range. This suggests that molecular  $\text{N}_2\text{O}$  does not adsorb on Pt{211} over the temperature range 120–300 K. This again supports the suggestion that the  $\text{N}_2\text{O}$  is formed on the surface during the TPD experiment.

So far, it has been assumed that  $\text{N}_2\text{O}$  is formed via the reaction of an adsorbed N atom with adsorbed NO. The second possible reaction mechanism for  $\text{N}_2\text{O}$  formation is via the formation of NO dimers, as shown below:



However, it is not thought that this reaction pathway leads to  $\text{N}_2\text{O}$  formation on Pt{211} as our previous RAIRS investigation<sup>16</sup> showed no evidence for the presence of  $(\text{NO})_2$  on the surface. In addition, DFT calculations<sup>16</sup> showed that the  $(\text{NO})_2$  species is very unstable on the Pt{211} surface. It is therefore assumed that  $\text{N}_2\text{O}$  forms on the Pt{211} surface via the reaction of an adsorbed N atom with adsorbed NO.

The dissociation of NO, and the reaction whereby  $\text{N}_2\text{O}$  is formed on the surface, leads to the production of adsorbed O atoms on the Pt{211} surface. It might be expected, therefore, that the desorption of  $\text{O}_2$  would be seen in the TPD spectrum. However, this was not the case in these or previous<sup>8</sup> TPD experiments. It has previously been speculated<sup>8,35</sup> that O atoms dissolve into the subsurface region of Pt{211} and  $\text{O}_2$  desorption only occurs once the subsurface sites have been saturated.<sup>8</sup> Hence, since no  $\text{O}_2$  desorption is observed here, it is assumed that the O atoms go into the subsurface region when the Pt{211} sample is heated. Previous experiments have shown that subsurface O atoms on the Pt surface desorb at around 1200 K (Ref. 35). The



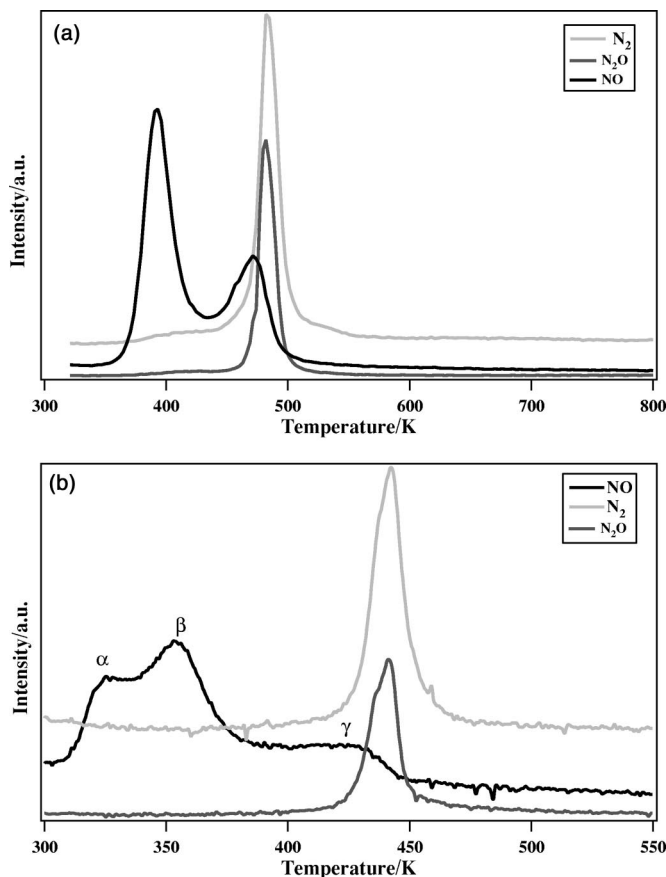


FIG. 4. (a) TPD spectra recorded following a 5 L NO dose onto Pt{211} at 330 K. The spectra shown are for the desorption of masses 28 (N<sub>2</sub>), 30 (NO), and 44 (N<sub>2</sub>O). The heating rate was 8 K s<sup>-1</sup>. (b) TPD spectra, recorded at a heating rate of 1 K s<sup>-1</sup>, for the same system following adsorption at 300 K. Note that the first NO peak, seen in (a), is now split into two peaks.

heating system used for the experiments reported here does not allow the sample to be heated above 1000 K in a TPD experiment, and hence the desorption of subsurface O atoms was not observable in these experiments.

## B. Room-temperature adsorption

TPD spectra were also recorded following NO adsorption at higher temperatures. Figure 4 shows TPD data recorded following a saturation dose of NO at 330 K [Fig. 4(a)] and 300 K [Fig. 4(b)]. Figure 4(a) was recorded at a heating rate of 8 K s<sup>-1</sup> and is therefore directly comparable to the spectra shown in Figs. 1 and 2. Unlike the spectra recorded following adsorption at 120 K, two NO desorption peaks are observed following adsorption at 330 K, with peak temperatures of 393 and 471 K. These NO TPD spectra are in good agreement with those previously recorded following NO adsorption on Pt{211} at room temperature.<sup>9</sup> Just as at 120 K, coincident desorption peaks for N<sub>2</sub> (mass 28) and N<sub>2</sub>O (mass 44) are observed at 482 K. In comparison with the spectra recorded following adsorption at 120 K, the ratio between the N<sub>2</sub> and N<sub>2</sub>O desorption peaks is rather different following NO adsorption at 330 K. At 120 K, the N<sub>2</sub> peak was approximately twice as large as the N<sub>2</sub>O peak. However, in the spectra shown in Fig. 4(a) the N<sub>2</sub> desorption peak is

only 1.4 times the size of the N<sub>2</sub>O peak. The observation of N<sub>2</sub> desorption following exposure of Pt{211} to NO is in agreement with previous observations,<sup>8,9</sup> however, N<sub>2</sub>O desorption has not been previously reported.

Since three NO desorption peaks were observed following adsorption at 120 K, but only two peaks were observed following adsorption at 330 K, it was decided to investigate this difference further. The room-temperature NO TPD experiments were repeated at a lower heating rate of 1 K s<sup>-1</sup>, to help to elucidate any further detail that may have been present in the desorption spectra. The sample was also dosed at a slightly lower temperature of 300 K. The spectra that result, following a saturation NO dose on Pt{211} at 300 K, are shown in Fig. 4(b). It is clear that the low-temperature NO peak, seen in Fig. 4(a), has split into two desorption peaks. Three NO peaks, at 324, 353, and ~427 K, are now observed. In addition, coincident peaks for N<sub>2</sub> and N<sub>2</sub>O desorption are also observed at 442 K. As for the TPD spectra shown in Figs. 1 and 2, the three NO peaks are labeled α, β, and γ, as it is thought that they are due to desorption of the same NO species observed following adsorption at 120 K. However, it is noted that the ratios of the α, β, and γ peaks are rather different following adsorption at 300 K, compared to 120 K. In particular, the β peak is the most intense peak following adsorption at 300 K, whereas the α peak is the most intense when adsorption occurs at 120 K. This spectrum is in disagreement with previous observations following NO adsorption at room temperature,<sup>9</sup> where only two NO TPD peaks were observed. However, as the α and β NO peaks are observed at 324 and 353 K, it is not expected that these peaks would be resolvable at a heating rate of 8 K s<sup>-1</sup>, as in the spectra in Fig. 4(a).

Figure 5 shows the way in which the NO, N<sub>2</sub>, and N<sub>2</sub>O peaks, seen in Fig. 4(b), grow into the TPD spectrum as a function of increasing NO dose at 300 K. The first peak observed to grow into the NO spectrum [Fig. 5(a)] is the γ peak, with a desorption temperature of 427 K. This peak grows in intensity very slightly with increasing NO dosage, and its desorption temperature remains constant. The second peak to grow into the NO spectrum, labeled β, grows in at 356 K. The desorption temperature of this peak decreases slightly with increasing NO dosage to reach 353 K at saturation, and it grows in intensity until it dominates the spectrum at saturation. The final peak to grow into the spectrum is that labeled α. This peak initially appears as a shoulder on the low-temperature side of the β peak at ~340 K. The peak grows in intensity and shifts down in temperature to reach 324 K at saturation. The N<sub>2</sub> [Fig. 5(b)] and N<sub>2</sub>O [Fig. 5(c)] desorption peaks both grow in intensity with increasing exposure of NO. The peaks are coincident at all NO doses and are initially observed at 475 K, shifting down in temperature with increasing exposure to reach 442 K following a saturation NO exposure.

As already stated, the three NO TPD peaks in Fig. 4(b) are assigned to the desorption of the same NO species as observed in the TPD following adsorption at 120 K (Figs. 1 and 2). Hence, the α-NO peak is assigned to the desorption of NO from the O-NO complex, the β-NO peak is assigned to the recombinative desorption of N and O atoms, and the



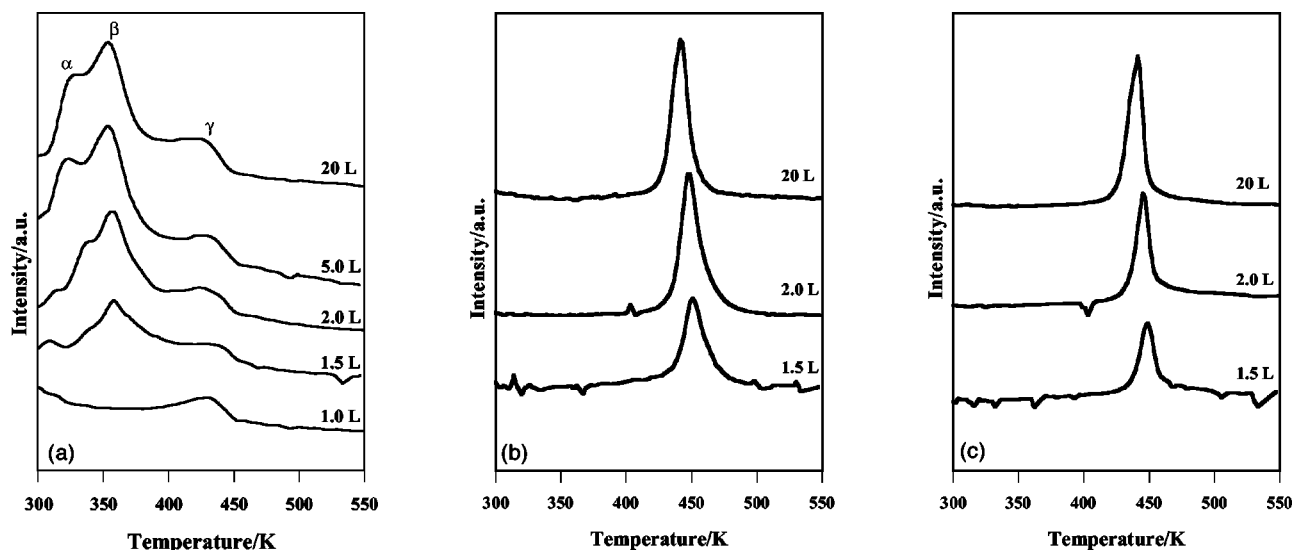


FIG. 5. TPD spectra following exposure of a Pt{211} surface held at 300 K to various exposures of NO. The spectra were recorded at a heating rate of  $1 \text{ K s}^{-1}$ . (a) shows the desorption of NO (mass 30), (b) shows the desorption of  $\text{N}_2$  (mass 28), and (c) shows the desorption of  $\text{N}_2\text{O}$  (mass 44). Note that the intensity scales on these spectra are arbitrary and therefore cannot be compared to one another.

$\gamma$ -NO peak is assigned to the desorption of step-bridged NO. Evidence that the TPD peaks are due to desorption of the same species as observed following adsorption at 120 K comes from a calculation of the desorption energies of the different species observed following adsorption at 120 K and 300 K. The Redhead equation<sup>36</sup> was used to calculate the desorption energies of the different species observed in the TPD spectra. Table II shows the results of these calculations. A preexponential factor of  $10^{14} \text{ s}^{-1}$  was used in these calculations. The errors given are those that result from allowing the preexponential factor to vary between  $10^{13}$  and  $10^{15} \text{ s}^{-1}$ . Note that these calculations only give approximate values for the desorption energy as an assumption has been made that the desorption process is first order—this is valid for the  $\alpha$ -NO and  $\gamma$ -NO species but is unlikely to be valid for the  $\beta$ -NO species. Note also that the Redhead equation assumes that the activation energy for desorption and the preexponential factor are coverage independent. It is clear from Table II that the calculations give very similar desorption energies for the  $\alpha$ -NO and  $\gamma$ -NO species, regardless of whether the adsorption occurred at 120 K or 300 K and regardless of the heating rates used in the two experiments. This implies that the TPD peaks in the two cases are, as suggested, due to the same NO species.

Although the same three NO desorption species are observed following adsorption at 120 K and 300 K, there are some differences between the TPD spectra recorded following adsorption at 120 K and those recorded following adsorption at 300 K. In contrast to the TPD spectra recorded following adsorption at 120 K (Figs. 1 and 2), it is the  $\beta$ -NO peak which dominates the TPD spectrum in Fig. 4(b). At 120 K, it was the  $\alpha$ -NO TPD peak which had the highest intensity. The  $\gamma$ -NO peak is also much smaller in the TPD spectrum that follows NO adsorption at 300 K [Fig. 4(b)]. It is likely that these differences are due to the dissociation that occurs on the surface when adsorption occurs at 300 K compared to 120 K. It has previously been shown<sup>16</sup> that NO dissociates on adsorption on Pt{211} at room temperature, but not at 120 K. Hence, in the 120 K experiments, NO dissociation only occurs as a result of heating during the TPD experiments. Since it is the step-bridged NO species that is thought to dissociate on the Pt{211} surface, increased amounts of NO dissociation would lead to a decrease in the amount of  $\gamma$ -NO observed in the TPD spectrum and an increase in the amount of  $\beta$ -NO. This is exactly what is seen in the TPD spectrum in Fig. 4(b). The  $\alpha$ -NO peak is also much smaller when adsorption occurs at 300 K, compared to when adsorption occurs at 120 K. This peak arises due to the de-

TABLE II. Calculated desorption energies for the various NO species observed in the TPD spectra in Figs. 1 and 4, following adsorption of NO on Pt{211} at various temperatures. The desorption energies  $E_d$  were calculated using the Redhead equation (Ref. 36) with a preexponential factor of  $10^{14} \text{ s}^{-1}$ . The errors given are those obtained if the preexponential factor is allowed to vary between  $10^{13}$  and  $10^{15} \text{ s}^{-1}$ . The adsorption temperature  $T$  and the heating rate  $\beta$  are also given.

	$T = 120 \text{ K}, \beta = 8 \text{ K s}^{-1}$		$T = 330 \text{ K}, \beta = 8 \text{ K s}^{-1}$		$T = 300 \text{ K}, \beta = 1 \text{ K s}^{-1}$	
	Desorption temperature (K)	$E_d$ (kJ mol <sup>-1</sup> )	Desorption temperature (K)	$E_d$ (kJ mol <sup>-1</sup> )	Desorption temperature (K)	$E_d$ (kJ mol <sup>-1</sup> )
$\alpha$ -NO	338	$91 \pm 6$			324	$93 \pm 6$
$\beta$ -NO	416	$113 \pm 8$	393	$107 \pm 8$	353	$102 \pm 7$
$\gamma$ -NO	503	$138 \pm 9$	471	$129 \pm 9$	427	$124 \pm 9$

sorption of NO from the NO–O complex. It is thought that this species is formed, following adsorption at 120 K, by the diffusion of terrace atop NO to the step edges where it bonds to an O atom in a step-bridge site.<sup>16</sup> There is no terrace atop NO formed on the surface when adsorption occurs at 300 K and hence less of the NO–O complex may form.

The TPD spectra in Fig. 4(a) show the desorption of only two NO species, in contrast to the three NO TPD peaks observed in the spectra shown in Fig. 4(b). This difference can be accounted for by the difference in heating rates used in each case. The spectra in Fig. 4(a) were recorded using a heating rate of  $8\text{ K s}^{-1}$  and those in Fig. 4(b) were recorded with a heating rate of  $1\text{ K s}^{-1}$ . It is clear that the lower heating rate allows the first TPD peak seen in Fig. 4(a) to be separated into two peaks. Hence, the disagreement between our TPD data in Fig. 4(b) and TPD data recorded previously<sup>9</sup> can be accounted for by the different heating rates used in the two experiments.

The NO TPD peaks in the spectrum in Fig. 4(a) can therefore be assigned to the desorption of step-bridged NO (the high-temperature peak) and to the desorption of NO from the O–NO complex and the recombinative desorption of N and O atoms (the lower-temperature peak). Confirmation of these assignments again comes from a calculation of the desorption energies of these species as seen in Table II. Table II shows that the peak which has been assigned to the desorption of step-bridged NO has a similar desorption energy in all three experiments—confirming that this TPD peak is due to desorption of the same species in all cases. The lower-temperature peak recorded following adsorption at 330 K, with a heating rate of  $8\text{ K s}^{-1}$  [Fig. 4(a)], has a desorption energy that falls exactly between that of the  $\alpha$ -NO and  $\beta$ -NO species that are observed following adsorption at 120 K. Hence, it is likely that this peak is due to a combination of these two peaks. Note that the calculations shown in Table II were performed only to investigate whether the TPD peaks in the three experiments were due to the same NO species. As we do not have an accurate value of  $A$ , the preexponential factor, the calculated values of the desorption energies are only approximate.

In both sets of spectra recorded following adsorption at room temperature [Figs. 4(a) and 4(b)], coincident desorption of  $\text{N}_2$  and  $\text{N}_2\text{O}$  is seen. However, the amount of  $\text{N}_2$  produced, compared to the  $\text{N}_2\text{O}$ , is much smaller in this case than in the spectra recorded following adsorption at 120 K. Since the  $\text{N}_2$  and  $\text{N}_2\text{O}$  peaks are still coincident, it is assumed that these two species are formed on the Pt{211} surface via the same mechanism as proposed for the TPD spectra recorded following adsorption at 120 K. Hence, the  $\text{N}_2\text{O}$  is assumed to form via the reaction of NO with N atoms. Some of the  $\text{N}_2\text{O}$  that is formed then desorbs and some dissociates to form gaseous  $\text{N}_2$  and adsorbed O atoms. Since NO dissociation is thought to occur on the Pt{211} surface at room temperature, but not at 120 K (Ref. 16), it is assumed that increased amounts of NO dissociation following adsorption at room temperature prevents the dissociation of  $\text{N}_2\text{O}$  on the surface and hence more of the  $\text{N}_2\text{O}$  desorbs intact. This would account for the smaller amounts of  $\text{N}_2$  desorption seen in the TPD spectra in Fig. 4 compared to in Fig. 1.

#### IV. SUMMARY AND CONCLUSIONS

TPD spectra have been recorded for NO adsorption on Pt{211} at 120, 300, and 330 K. Adsorption of NO at 120 K leads to the production of three NO TPD peaks along with coincident peaks for  $\text{N}_2$  and  $\text{N}_2\text{O}$  desorption. These spectra are in excellent agreement with previous data recorded for NO adsorption on Pt{211} at 95 K (Ref. 8). In disagreement with previous data,<sup>9</sup> TPD spectra recorded at a heating rate of  $1\text{ K s}^{-1}$ , following adsorption at 300 K, also show the desorption of three NO species. However, TPD spectra recorded following adsorption at 330 K, with a heating rate of  $8\text{ K s}^{-1}$ , are in good agreement with those observed previously.<sup>9</sup> This difference can be assigned to the different heating rates used in the two experiments.

Although our spectra are in good agreement with previous data, the assignments made here are in contrast to those made previously.<sup>8,9</sup> The three NO TPD peaks observed following adsorption at 95 K (Ref. 8) have been previously assigned to desorption of NO from the step edges (the high-temperature peak) and the terraces (the two low-temperature peaks). For the room-temperature data,<sup>9</sup> again the high-temperature peak was assigned to the desorption of NO from the step sites and the low-temperature peak was assigned to NO desorption from the terraces. By using a combination of our TPD data and previous RAIRS and DFT data,<sup>16</sup> we have shown that none of the peaks observed in the NO TPD spectrum can be assigned to the desorption of molecular NO from the terraces of Pt{211}. Evidence for this comes from the fact that none of the NO TPD peaks for Pt{211} occur at the same desorption temperature as those observed for Pt{111} (Refs. 17–24). For CO adsorption on Pt{211}, where TPD peaks can be successfully assigned to the desorption of step and terrace CO species,<sup>30</sup> the terrace species have the same desorption temperature as observed for Pt{111}. Hence, previous assignments of TPD spectra for NO on Pt{211} need to be reconsidered.<sup>8,9</sup> Previous TPD investigations of NO adsorption on Pt{533} (Refs. 27–29) showed the desorption of four NO species. As for Pt{211}, the high-temperature peak was assigned to NO desorption from the step sites and the three low-temperature peaks were assigned to NO desorption from the terraces. In light of the results presented here for NO adsorption on Pt{211}, it is possible that the TPD assignments for the NO/Pt{533} system may also need reconsideration.

The observation of  $\text{N}_2$  and  $\text{N}_2\text{O}$  desorption in the TPD experiments gives evidence for the occurrence of NO dissociation on the Pt{211} surface. Previous TPD measurements on the flat Pt{111} surface<sup>17–24</sup> have not shown any evidence for the dissociation of NO, either during adsorption or during the TPD experiment. Hence, as expected, the dissociation of NO on Pt{211} is mediated by the presence of the step sites on the surface.

The  $\text{N}_2\text{O}$  that is formed on Pt{211} has been shown to be formed via the reaction of NO with adsorbed N atoms. The  $\text{N}_2\text{O}$  then partly desorbs and partly dissociates to give gaseous  $\text{N}_2$  and adsorbed O atoms. The production of  $\text{N}_2$  from  $\text{N}_2\text{O}$ , rather than from an N atom recombination reaction, causes the  $\text{N}_2$  and  $\text{N}_2\text{O}$  desorption to be coincident. In agreement with previous observations, no desorption of  $\text{O}_2$  is seen

at any time in the TPD experiments. This occurs as a result of the O atoms dissolving into the subsurface region on heating.

The standard model for adsorption on stepped surfaces consists of sequential “step then terrace” adsorption. This has previously been shown to be valid for CO adsorption on Pt{211} (Refs. 30 and 31); however, as we have shown here and in a previous RAIRS and DFT investigation,<sup>16</sup> much more care must be taken when applying this model to NO adsorption on Pt{211}. The occurrence of NO dissociation on Pt{211} causes this adsorption system to be much more complicated than that of CO adsorption on Pt{211}. Hence, as already shown, TPD peaks observed following NO adsorption on Pt{211} cannot be simply assigned to the desorption of step and terrace NO species. The simplicity of the sequential adsorption model has also been shown to break down for NO adsorption on Pd{211} (Refs. 37–39).

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